

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 988 790 A1**

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
29.03.2000 Bulletin 2000/13

(21) Application number: 99307521.7

(22) Date of filing: 23.09.1999

(51) Int Cl.7: **A01N 43/90**

// (A01N43/90, 59:20, 59:02,  
47:44, 47:38, 47:14, 47:04,  
43:84, 43:76, 43:653, 43:60,  
43:54, 43:42, 43:40, 43:36,  
43:32, 37:50, 37:38, 37:34,  
37:22)

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: 25.09.1998 US 160310

(71) Applicant: **American Cyanamid Company**  
Madison, New Jersey 07940-0874 (US)

(72) Inventors:  
• **Cotter, Henry van Tuyt**  
Trenton, New Jersey 08618 (US)

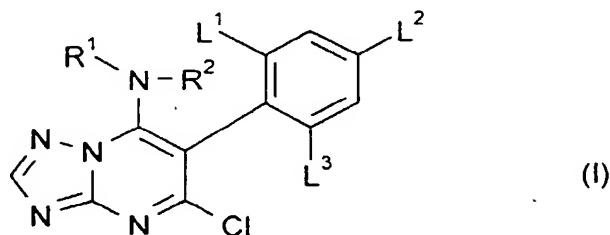
• **May, Leslie Francis**  
Wokingham, Berkshire RG41 1JJ (GB)  
• **Reichert, Gunter**  
55270 Bubenheim (DE)  
• **Sieverding, Ewald**  
55278 St. Johann (DE)

(74) Representative: **Walters, Philip Bernard William**  
Wyeth Laboratories,  
Patents & Trade Marks Department,  
Huntercombe Lane South,  
Taplow  
Maidenhead, Berkshire SL6 0PH (GB)

(54) **Fungicidal mixtures**

(57) Fungicidal compositions comprising an acceptable carrier and/or surface active agent and synergistically effective amounts of

(a) at least one azolopyrimidine of formula I



in which

R<sup>1</sup>, R<sup>2</sup>, L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup> have the meaning given in claim 1; and

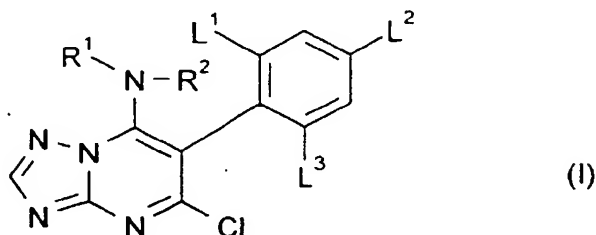
(b) at least one fungicidal active ingredient selected from benomyl, carboxin, captan, chlorothalonil, copper oxychloride, cyprodinil, dimethomorph, dithianon, dodine, famoxadone, fenhexamid, fenpiclonil, fenpropimorph, fludioxonil, mancozeb, metalaxyl, pyrimethanil, quinoxifen, sulfur, triforine, vinclozolin, a fungicidal triazole derivative, and a synthetic strobilurine derivative. The invention also provides a method of controlling the growth of phytopathogenic fungi at a locus by applying synergistically effective amounts of at least one azolopyrimidine of formula I and at least one fungicidal active ingredient (b) to the locus.

EP 0 988 790 A1

## Description

## BACKGROUND OF THE INVENTION

[0001] The present invention relates to a fungicidal composition comprising a fungicidally acceptable carrier and/or surface active agent and synergistically effective amounts of  
(a) at least one azolopyrimidine of formula I



in which

- R<sup>1</sup> represents a C<sub>1-6</sub> alkyl, C<sub>3-6</sub> alkenyl or C<sub>1-6</sub> haloalkyl group, or  
 R<sup>2</sup> represents a hydrogen atom or a C<sub>1-6</sub> alkyl group, or  
 R<sup>1</sup> and R<sup>2</sup> taken together represent a C<sub>3-8</sub> alkylene group,  
 L<sup>1</sup> represents a halogen atom;  
 L<sup>2</sup> and L<sup>3</sup> each independently represent a hydrogen or a halogen atom; and

and at least one fungicidal active ingredient selected from the following classes (A), (B) and (C):

- (A) a compound selected from the group consisting of beriomyl, carboxin, captan, chlorothalonil, copper oxychloride, cyprodinil, dimethomorph, dithianon, dodine, famoxadone, fenpiclonil, fenpropimorph, fluazinam, mancozeb, metalaxyl, pyrimethanil, quinoxifen, sulfur, triforine and vinclozolin;  
 (B) a fungicidal triazole derivative; and  
 (C) a synthetic strobilurine derivative.

[0002] The fungicidal compounds of formula I to be used according to the present invention are known from US patent US 5,593,996. The compounds of the classes (A) and (B) are known from "The Pesticide Manual", 11<sup>th</sup> edition (1997), Editor Clive Tomlin. Fenhexamid is known from AGROW No. 287, p. 21. The synthetic strobilurines are known, for example, from WO 92/08703, EP 0 253 213 and EP 0 398 692.

[0003] However, none of the above mentioned prior art references teaches a combination of compounds of formula I with any of the fungicidal active ingredients selected from the classes (A), (B) and (C) as described above, nor that such mixtures show synergistic effects and can advantageously be used for controlling diseases such as wheat powdery mildew, barley powdery mildew, wheat leaf rust, barley net blotch and wheat Septoria leaf blotch, Botrytis diseases and others.

[0004] Surprisingly, when compounds of formula I were tank mixed with compounds from classes (A), (B) and (C) and used in greenhouse and field trials, a synergistic increases in activity were observed, compared to the activity expected based on the activities of the individual active ingredients.

[0005] A mixture of fungicides shows synergistic effect if the fungicidal activity of the mixture is larger than the sum of activities of the separately applied compounds. The expected fungicidal activity for a given mixture of two fungicides can also be calculated as follows (See Colby, S.R., "Calculating synergistic and antagonistic response of herbicide combinations", Weeds 15, pp 20-22 (1967):

$$EE = x + y - x y / 100$$

wherein

x is the efficacy in % compared with an untreated control upon treatment with a fungicidal active ingredient A at a dose rate a;

y is the efficacy in % compared with an untreated control upon treatment with a fungicidal active ingredient B at a dose rate b;

EE is the expected efficacy with a combination of fungicidal active ingredients A and B at a dose of a + b, respectively.

[0006] If the actual efficacy (E) exceeds the expected (calculated) one (EE), the mixture displays a synergistic effect.

#### SUMMARY OF THE INVENTION

[0007] The present invention includes a fungicidal composition comprising an acceptable carrier and/or surface active agent and synergistically effective amounts of at least one compound of formula I, and at least one fungicidal active ingredient selected from the following classes (A), (B) and (C):

(A) a compound selected from the group consisting of benomyl, carboxin, captan, chlorothalonil, copper oxychloride, cyprodinil, dimethomorph, dithianon, dodine, famoxadone, fenpiclonil, fenpropimorph, fluazinam, mancozeb, metalaxyl, pyrimethanil, quinoxifen, sulfur, triforine and vinclozolin;

(B) a fungicidal triazole derivative; and

(C) a synthetic strobilurine derivative.

[0008] The present invention also includes a method of controlling the growth of phytopathogenic fungi at a locus which comprises applying synergistically effective amounts of at least one azolopyrimidine of formula I and at least one fungicidally active ingredient selected from classes (A), (B) and (C) defined above to the locus.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] Preferred compounds of formula I are those wherein

R<sup>1</sup> and R<sup>2</sup> together with the interjacent nitrogen atom represent a 4-methylpiperidine ring, or wherein

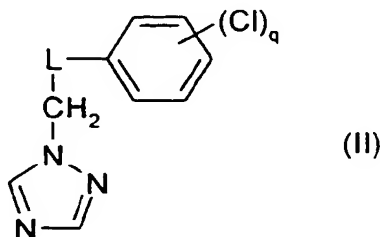
R<sup>1</sup> represents a C<sub>1-6</sub> alkyl, in particular an isopropyl group, a C<sub>1-6</sub> haloalkyl, in particular a 2,2,2-trifluoroethyl or a 1,1,1-trifluoroprop-2-yl group, or a

C<sub>3-8</sub> cycloalkyl group, in particular a cyclopentyl or cyclohexyl group and R<sup>2</sup> represents a hydrogen atom, and/or wherein L<sup>1</sup> represents a fluorine or chlorine atom and L<sup>2</sup> and L<sup>3</sup> each independently represent a hydrogen atom or a fluorine atom, in particular

wherein L<sup>1</sup> represents fluorine, L<sup>2</sup> represents hydrogen and L<sup>3</sup> represents chlorine or wherein L<sup>1</sup> through L<sup>3</sup> represent fluorine.

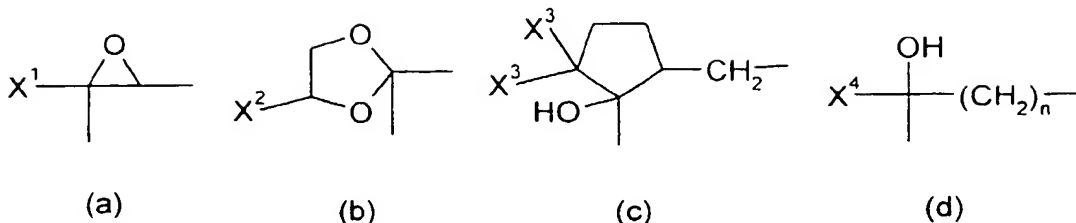
[0010] Particularly preferred are the following azolopyrimidines: 5-chloro-6-(2-chloro-6-fluorophenyl)-7-(4-methylpiperid-1-yl)-[1,2,4]triazolo[1,5-a]pyrimidine coded Azolopyrimidine A, 5-chloro-6-(2-chloro-6-fluorophenyl)-7-(2,2,2-trifluoroethylaminol-[1,2,4]triazolo[1,5-a]pyrimidine coded Azolopyrimidine B and 5-chloro-6-(2,4,6-trifluorophenyl)-7-(1,1,1-trifluoroprop-2-ylamino)-[1,2,4]triazolo[1,5-a]pyrimidine coded Azolopyrimidine C. Azolopyrimidine C due to the chirality of its 1,1,1-trifluoroprop-2-yl group may be applied as a racemic mixture or in the form of an enantiomeric enriched compound, in particular as (S)-enantiomer coded (S)-Azolopyrimidine C.

[0011] Preferred triazole derivatives in the practice of this invention are the compounds of formula II,



wherein

L represents a linking group selected from the groups (a), (b), (c) and (d)

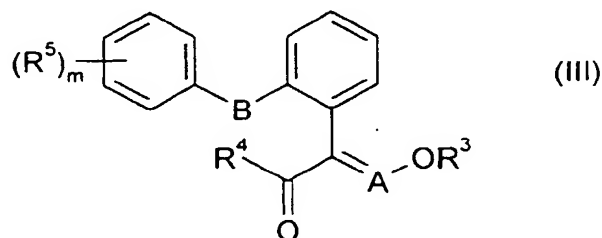


10 in which

15  $X^1$  represents an alkyl or an optionally substituted phenyl group;  
 $X^2$  and  $X^3$  each independently represent a hydrogen atom or an alkyl group;  
 $X^4$  represents an alkyl or cyclopropylalkyl group;  
 $q$  is 1 or 2; and  
 $n$  is 0 or 2.

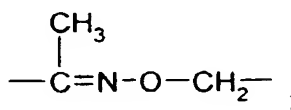
20 **[0012]** Particularly preferred are the triazoles selected from the group consisting of cyproconazole, epoxiconazole, metconazole, propiconazole and tebuconazole.

**[0013]** Preferred strobilurine derivatives in the practice of this invention are the compounds of formula III,



30 wherein

35 A represents N or CH;  
 B represents a -O-, -OCH<sub>2</sub>-, a -CH<sub>2</sub>O-, a pyrimid-4,6-dioxydiyl group or a group of formula



45  $R^3$  represents a C<sub>1-4</sub> alkyl group;  
 $R^4$  represents a C<sub>1-6</sub> alkoxy or a C<sub>1-6</sub> alkylamino group;  
 $R^5$  represents a hydrogen or halogen atom or a cyano, a C<sub>1-4</sub> alkyl or a C<sub>1-4</sub> haloalkyl group; and  
 $m$  is 0, 1 or 2;  
 in particular azoxystrobin, kresoxim methyl, CGA-279202 (AGROW 279, p.17 1998) or SSF126 (Pesticide Manual,  
 50 loc. cit., page 1114)

**[0014]** Preferred compositions of this invention comprise the following constituents:

- 55
- a carrier agent;
  - at least one azolopyrimidine of formula I,
  - at least one compound selected from the classes (A), (B) and (C) as defined above;
  - optionally an adjuvant selected from the group consisting of polyalkoxylated alcohols, triglycerides and amines, in particular Synperonic 91-6, which is commercially available from ICI Surfactants;

- optionally a foam breaking agent, in particular a mixture of perfluoroalkylphosphonic acids and/or perfluoroalkylphosphinic acids, in particular Defoamer SF or Fluowett PL, which are commercially available from Clariant GmbH.

**[0015]** The compound of formula I and the compound selected from the classes (A), (B) and (C) as defined above are to be applied together, in synergistically effective amounts. These synergistic mixtures exhibit an extraordinary efficacy against a broad range of phytopathogenic fungi, in particular against fungi from the classes ascomycetes, basidiomycetes, oomycetes and deuteromycetes. Therefore, they can be applied advantageously against a broad range of diseases in different crops. They may be applied as leaf, stem, root, into-water, seed dressing, nursery box or soil fungicides.

**[0016]** The composition according to the invention may be preferably applied for controlling phytopathogenic fungi of the genera: Achlya, Alternaria, Balansia, Bipolaris, Blumeria (Erysiphe), Cercospora, Cochliobolus, Curvularia, Cy lindrocladium, Drechslera, Entyloma, Fusarium, Gaeumannomyces, Gerlachia, Gibberella, Guignardia, Leptosphaeria, Magnaporthe, Mucor, Mycosphaerella, Myrothecium, Nigrospora, Peronospora, Phoma, Pseudoperonospora, Pseudocercospora, Phytophthora, Puccinia, Pyricularia, Pythium, Rhizoctonia, Rhizopus, Sarocladium, Sclerophthora, Sclerotium, Septoria, Tilletia, Uncinula, Ustilago, Ustilaginoidea, and Venturia, in particular the species Blumeria graminis f. sp. tritici, Botrytis cinerea, Septoria tritici Erysiphe cichoracearum and Puccinia recondita.

**[0017]** The compositions according to the invention are preferably applied for controlling the above phytopathogenic fungi on monocotyledonous plants, such as barley and wheat, rice and turf grasses, or fruit crops such as pomefruits, stonefruits and vines, as well as all kinds of vegetables, oil and oil seed crops, and ornamentals.

**[0018]** The application rate of the compound of formula I according to this invention is suitably in the range of 1 to 2000 grams of active ingredient (g a.i.) per hectare, with rates between 20-500 g a.i./ha often achieving satisfactory control. The optimal rate for a specific application will depend on the crop(s) under cultivation and the predominant species of infesting fungi, and readily may be determined by established biological tests known to those skilled in the art.

**[0019]** In general, the preferred application rate of the compounds of formula I is in the approximate range of 10 to 500 g a.i./ha, more preferably 20-300 g a.i./ha.

**[0020]** The optimal rate for the compounds of classes (A), (B) and (C), will, however, depend on the crop(s) under cultivation and the level of infestation by the fungus, and can readily be determined by established biological tests.

**[0021]** The approximate ratio (by weight) of the compound of formula I to the fungicidal active ingredient of the classes (A), (B) and (C) is suitably from 1:100 to 100:1. The preferred ratio formula I : (A), (B) or (C) may vary, e.g., from about 1 : 50 to about 50 : 1, in particular from about 1 : 4 to about 4 : 1, most preferably from 1 : 1.5 to 1.5 : 1.

**[0022]** The active compounds can be co-formulated together in a suitable ratio according to the present invention, together with carriers and/or additives known in the art.

**[0023]** A method of making such a composition is also provided which comprises bringing the compound of formula I and the fungicidal active ingredient selected from the classes (A), (B) and (C) as defined above into association with at least one carrier. It is also envisaged that different isomers or mixtures of isomers of formula I and/or the fungicidal active ingredient selected from the classes (A), (B) and (C) may have different levels or spectra of activity and thus compositions may comprise individual isomers or mixtures of isomers.

**[0024]** A composition according to the invention preferably contains from 0.1 % to 99.9%, preferably 0.2 to 80 % by weight (w/w) of active ingredients.

**[0025]** A carrier in a composition according to the invention may be any material with which the active ingredients may be formulated to facilitate application to the locus to be treated (which may, for example, be a plant, seed, foliage, soil, or into the water where the plant grow or to the roots), or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally a gas but which has been compressed to form a liquid.

**[0026]** The compositions may be manufactured into, e.g., emulsion or emulsifiable concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, aerosols, water dispersible granules, tablets, micro-capsules, gels and other formulation types by well-established procedures. These procedures may include intensive mixing and/or milling of the active ingredients with other substances, such as fillers, solvents, solid carriers, surface active compounds (surfactants), and, optionally solid and/or liquid auxiliaries and/or adjuvants. The form of application such as spraying, atomizing, dispersing or pouring may be chosen like the compositions according to the desired objectives and the given circumstances.

**[0027]** Solvents used in the composition of this invention may be aromatic hydrocarbons, e.g. Solvesso® 200, substituted naphthalenes, phthalic acid esters, such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, or  $\gamma$ -butyrolactone, higher alkyl pyrrolidones, e.g. n-octylpyrrolidone or cyclohexylpyrrolidone, epoxidized plant oil esters, e.g. methylated coconut or soybean oil ester and water. Mixtures of different solvents may be suitable.

**[0028]** Solid carriers used in the composition of this invention which may be used for dusts, wettable powders, water dispersible granules, or granules, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite or attapulgite or

others. The physical properties may be improved by addition of highly dispersed silica gel or polymers. Carriers for granules may be porous material, e.g., pumice, kaolin, sepiolite, bentonite; non-sorptive carriers may be calcite or sand or others. Additionally, a multitude of pre-granulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

5 [0029] Pesticidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surfactant facilitates this process of dilution. Thus, preferably at least one carrier in a composition according to the invention is a surfactant. For example, the composition may contain two or more carriers, at least one of which is a surfactant.

10 [0030] Surfactants may be nonionic, anionic, cationic or zwitterionic substances with good dispersing, emulsifying and wetting properties, depending on the nature of the active ingredients to be formulated. Surfactants may also include mixtures of individual surfactants.

15 [0031] Wettable powders in this invention suitably may contain about 5 to 90% w/w of active ingredient and, in addition to solid inert carrier, about 3 to 10% w/w of dispersing and wetting agents and, where necessary, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers. Dusts may be formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition containing about 0.5 to 10% w/w of active ingredient. Water dispersible granules and granules may have a size approximately between 0.15 mm and 2.0 mm, and may be manufactured by a variety of techniques known in the art. These granules suitably will contain about 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizer, surfactants, slow release modifiers and binding agents. Emulsifiable concentrates suitably may contain, in addition to a solvent or a mixture of solvents, approximately 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives, such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates may be milled so as to obtain a stable, non-sedimenting flowable product and suitably contain about 5 to 75% w/v active ingredient, and 0.5 to 15% w/v of dispersing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystallization or as antifreeze agents.

20 [0032] Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

30 [0033] The invention also encompasses the use of a carrier which will provide slow release of the pesticidal compounds into the environment of a plant which is to be protected, to extend the duration of the protective activity of the composition.

35 [0034] The biological activity of the active ingredients may be increased by including an adjuvant in the formulation or a spray dilution. An adjuvant is defined here as a substance which can increase the biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation as a coformulant or carrier, or can be added to the spray tank together with the formulation containing the active ingredient.

[0035] As a commodity, the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to about 0.001% of active ingredient. The doses preferably are in the approximate range from 0.01 to 10 kg a.i./ha.

40 [0036] Examples of formulations useful in the practice of the invention are:

EP 0 988 790 A1

SC-I 1		
active ingredient	Azolopyrimidine C	100.0 g
Dispersing agent	Morwet D425 <sup>1)</sup>	25.0 g
Dispersing agent	Pluronic® PE10500 <sup>2)</sup>	5.0 g
Antifoaming agent	Rhodorsil® 426R <sup>3)</sup>	1.5 g
Dispersing agent	Rhodopol® 23 <sup>3)</sup>	2.0 g
Antifreezing agent	Propylene glycol	80.0 g
Biocidal agent	Proxel® GXL <sup>4)</sup>	1.0 g
Water		to 1000 ml
SC-I 2		
active ingredient	Azolopyrimidine C	100.0 g
Dispersing agent	Soprophor® FL <sup>3)</sup>	30.0 g
Antifoaming agent	Rhodorsil® 426R <sup>3)</sup>	1.5 g
Dispersing agent	Rhodopol® 23 <sup>3)</sup>	2.0 g
Antifreezing agent	Propylene glycol	80.0 g
Biocidal agent	Proxe l® GXL <sup>4)</sup>	1.0 g
Water		to 1000 ml
SC-A/B/C		
active ingredient	selected from classes (A), (B), (C)	200.0 g
Dispersing agent	Soprophor® FL <sup>3)</sup>	25.0 g
Antifoaming agent	Rhodorsil® 426R <sup>3)</sup>	1.5 g
Dispersing agent	Rhodopol® 23 <sup>3)</sup>	2.0 g
Antifreezing agent	Propylene glycol	80.0 g
Biocidal agent	Proxel® GXL <sup>4)</sup>	1.0 g
Water		to 1000 ml
SC-I + A/B/C		
active ingredient	Azolopyrimidine C	60.0 g
active ingredient	selected from classes (A), (B) and (C)	120.0 g
Dispersing agent	Soprophor® FL <sup>3)</sup>	25.0 g
Antifoaming agent	Rhodorsil® 426R <sup>3)</sup>	1.5 g
Dispersing agent	Rhodopol® 23 <sup>3)</sup>	2.0 g
Antifreezing agent	Propylene glycol	80.0 g
Biocidal agent	Proxel® GXL <sup>4)</sup>	1.0 g
Water		to 1000 ml
DC-I 1		
active ingredient	Azolopyrimidine A	100.0 g
Wetting agent	Pluronic® PE6400 <sup>2)</sup>	50.0 g
Dispersing agent	Lutensol® TO 12 <sup>2)</sup>	50.0 g
Solvent	benzyl alcohol	to 1000 ml

<sup>1)</sup> Product commercially available from Witco

<sup>2)</sup> Product commercially available from BASF AG, Germany

<sup>3)</sup> Product commercially available from Rhône-Poulenc

<sup>4)</sup> Product commercially available from Zeneca

[0037] The formulation SC-A/B/C, comprising a compound selected from the classes (A), (B) and (C), may be mixed with any of the other formulations SC-I 1, SC-I 2, SC-I 3, or DC-I which comprise the Azolopyrimidine C to produce a composition of this invention.

[0038] In a preferred embodiment of the invention, each active ingredient is added to a tank mix in a separate formulation, to form a composition of this invention.

[0039] The present invention also relates to a kit for the preparation of a spray mixture consisting of two separate units:

(i) a unit which comprises at least one azolopyrimidine of formula I, in particular one or more compounds selected from the Azolopyrimidines A, B or C, conventional carriers and optionally adjuvants;

(ii) a unit which comprises at least one active ingredient selected from the classes (A), (B) and (C), preferably one or more compounds selected from the group consisting of carboxin, fluazinam, quinoxifen, metalaxyl, famoxadone, metconazole, epoxiconazole, propiconazole, azoxystrobin or kresoxim methyl conventional carriers and optionally adjuvants.

[0040] In a preferred embodiment, the kit includes two bottles with dispensing means which allow the easy and correct addition of the active ingredients to the tank mix.

[0041] A composition according to the invention preferably contains from about 0.5% to 95% by weight of active ingredients.

[0042] The compositions of this invention may be diluted down to a concentration of about 0.0001% of active ingredients.

[0043] The compositions of this invention can be applied to the plants or their environment simultaneously with or in succession with other active substances. These other active substances can be either fertilizers, agents which donate trace elements, or other preparations which influence plant growth. However, they can also be other fungicides, selective herbicides, insecticides, bactericides, nematocides, algicides, molluscicides, rodenticides, virucides, compounds inducing resistance into plants, biological control agents such as viruses, bacteria, nematodes, fungi and other micro-organisms, repellents of birds and animals, and plant growth regulators, or mixtures of several of these preparations, if appropriate together with other carrier substances conventionally used in the art of formulation, surfactants or other additives which promote application.

[0044] Examples of insecticidal compounds useful in this invention are alpha-cypermethrin, benfuracarb, BPMC, buprofezine, carbosulfan, cartap, chlorfenvinphos, chlorpyrifos-methyl, cycloprothrin, cypermethrin, esfenvalerate, ethofenprox, fenpropathrin, flucythrinate, flufenoxuron, hydramethylnon, imidacloprid, isoxathion, MEP, MPP, nitenpyram, PAP, permethrin, propaphos, pymetrozine, silafluofen, tebufenozide, teflubenzuron, temephos, terbufos, tetra-chlorvinphos and triazamate.

[0045] Examples of biological control agents useful in this invention are: *Bacillus thuringiensis*, *Verticillium lecanii*, *Autographica californica* NPV, *Beauveria bassiana*, *Ampelomyces quisqualis*, *Bacillus subtilis*, *Pseudomonas fluorescens*, *Steptomyces griseoviridis* and *Trichoderma harzianum*.

[0046] Examples of chemical agents that induce systemic acquired resistance in plants are: isonicotinic acid or derivatives thereof, 2,2-dichloro-3,3-dimethylcyclopropylcarboxylic acid and BION.

[0047] The present invention is of wide applicability in the protection of crops, trees, residential and ornamental plants against fungal attack. Preferred crops are cereals, such as wheat and barley, rice, vines, and apples. The duration of the protection is normally dependent on the individual compound selected, and also a variety of external factors, such as climate, the impact of which may be mitigated by the use of a suitable formulation.

[0048] The following examples further illustrate the present invention. It should be understood, however, that the invention is not limited solely to the particular examples given below.

## EXAMPLES

### General Methods

[0049] The trials are carried out under greenhouse (Examples 1 to 32) or field conditions (Examples 33 to 40) in residual or curative applications. The fungicides are applied in single treatments, or in a combination comprising an azolopyrimidine of formula I and a compound selected from the classes (A), (B) and (C) as defined above. The compounds are applied in form of an aqueous spray mix obtained from a concentrated formulation or the technical material.

I. Cereals and Dicots - Greenhouse**[0050]**

1. Seed is planted in 6 cm diameter plastic pots and maintained in the greenhouse.
2. When the primary leaf is fully expanded in the case of cereals or several leaves are present in the case of dicots, formulated test compounds are sprayed with a three nozzle overhead fungicide sprayer to near run-off. Alternatively, a single nozzle overhead track sprayer is used for application of the compounds to cereals at a rate of 200 l/ha. Plants are then allowed to air-dry.
3. Inoculation precedes treatment in the case of curative evaluations and follows treatment in case of residual evaluations. For inoculation of powdery mildew disease, plants are set up on greenhouse benches with bottom watering mats and-inoculated by dusting them with conidia from infected plants. Between inoculation and treatment for curative evaluations and between treatment and inoculation for residual evaluations, plants are maintained in the greenhouse with bottom watering.
- For inoculation of non-powdery mildew diseases, an aqueous spore suspension of the pathogen is applied to the plant and the plants are kept 1-2 days in a moist infection chamber before being returned to the greenhouse where they are maintained by bottom watering.
4. Disease on the foliage as percent leaf area with disease symptoms/signs is evaluated about 7 days after inoculation. In the case of wheat, the tips and bases of the leaves are excluded from the evaluation.

$$\% \text{ disease control} = 100 - \frac{\% \text{ disease in treated plants}}{\% \text{ disease in untreated plants}} \times 100\%$$

**FORMULATION, REFERENCE COMPOUNDS AND CONTROLS:****[0051]**

1. Technical compounds are formulated in a solvent/surfactant system consisting of 5% acetone and 0.05% Tween 20 in deionized water. Compounds are dissolved in acetone prior to addition of the water; the Tween 20 can be added through either the acetone or the water. Dilutions are made using the solvent/surfactant system. Formulated compounds are prepared using deionized water.
2. Two kinds of controls are included:  
Plants treated with the solvent/surfactant solution and inoculated (Solvent Blank).  
Untreated plants which are inoculated (Inoculated Control).

**[0052]** For the field study formulated Azolopyrimidine A, B or C and formulated compounds from the classes (A), (B) and (C) were used.

Evaluation of the disease:

**[0053]** Assessments of the diseases took place at the indicated day after the application of the compounds. Per cent infected leaf area infected was evaluated. The efficacy of the compounds/compounds mixtures to control the diseases was calculated by using the formula given above under item 4:

II. Apple Fruit Botrytis**[0054]**

1. Apples (*Malus X domestica* Borkh.) variety Golden Delicious are disinfected by washing them briefly in 70 % ethanol. After drying the apples are marked with four short equal-distant lines indicating the positions to be wounded.
2. Corresponding with the marks, four holes are poked around the apple equator with a pipette tip. 10 µl of the treatment solution are pipetted into each hole.
3. Three hours after application, 10 µl of a conidial suspension of *Botrytis cinerea* are pipetted into each. For incubation, the treated/inoculated apples are set up for five days.
4. Disease occurs as rotten apple tissue surrounding the inoculated wounds. The diameter of the rotten zone around each wound is measured.

## FORMULATION, REFERENCE COMPOUNDS AND CONTROLS:

**[0055]**

1. Technical compounds are formulated in a solvent system consisting of 5% acetone and 0.05% Tween 20 in deionized water. Compounds are dissolved in acetone prior to dilution with water. Formulated compounds are prepared using deionized water.

2. Three kinds of controls are included:

Apples treated with the solvent solution and inoculated (Solvent Blank).

Untreated apples which are inoculated (Inoculated Control).

Untreated apples which are not inoculated (Uninoculated Control).

Evaluation of the disease:

Assessments of the diseases took place at the indicated day after the application of the compounds. Per cent infected leaf area infected was evaluated. The efficacy of the compounds/compounds mixtures to control the diseases was calculated by using the formula:

$$\% \text{ disease control} = 100 - \frac{\text{mean of diameters on treated apples}}{\text{mean of diameters on untreated apples}} \times 100\%$$

Determination of synergy:

Synergy was calculated using the % disease control values of specific treatments for the two COLBY formula given hereinabove

III. Field Tests

The compounds are applied according to good agricultural practice in the form of an aqueous spray mix obtained from a concentrated formulation or the technical material at a rate of 400 l/ha. The disease control is evaluated according to the formula given for the greenhouse tests.

A Greenhouse TestsExample 1

Fungicidal efficacy of the mixture of Azolopyrimidine A + fenpropimorph (3 day residual) against *Leptosphaeria nodorum* on wheat

The tank mix was obtained from technical material of Azolopyrimidine A and an EC formulation containing 750 g fenpropimorph per liter. The observed and expected efficacies with different rates are given in Table I:

Table I

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine A	fenpropimorph		
100	0	40	--
10	0	35	--
0	5	15	--
0	0.5	19	--
100	5	71	49
100	0.5	80	51
10	5	55	45
10	0.5	50	47

Example 2

[0059] Fungicidal efficacy of the mixture of Azolopyrimidine A + tebuconazole (3 day residual) against *Leptosphaeria nodorum* on wheat. The tank mix was obtained from technical material of Azolopyrimidine A and an EC formulation containing 250 g tebuconazole per liter. The observed and expected efficacies with different rates are given in Table II:

Table II

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine A	tebuconazole		
100	0	40	--
0	0.2	19	--
0	0.02	25	--
100	0.2	88	51
100	0.02	87	55

Example 3

[0060] Fungicidal efficacy of the mixture of Azolopyrimidine A + tebuconazole (2 day residual) against *Blumeria graminis* on wheat

The tank mix was obtained from technical material of Azolopyrimidine A and an EC formulation containing 250 g tebuconazole per liter. The observed and expected efficacies with different rates are given in Table III:

Table III

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine A	tebuconazole		
10	0	14	--
0	0.2	9	--
0	0.02	2	--
10	0.2	52	22
10	0.02	33	16

Example 4

[0061] Fungicidal efficacy of the mixture of Azolopyrimidine A + vinclozolin (3 day residual) against *Botrytis cinerea* on apple fruits

The tank mix was obtained from technical material of Azolopyrimidine A and a WG formulation containing 500 g vinclozolin per kg. The observed and expected efficacies with different rates are given in Table IV:

Table IV

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine A	vinclozolin		
10	0	33	--
1	0	0	--
0	10	8	--
10	10	54	38
1	10	31	8

Example 5

[0062] Fungicidal efficacy of the mixture of Azolopyrimidine A + cyprodinil (3 day residual) against *Botrytis cinerea*

on apple fruits

The tank mix was obtained from technical material of Azolopyrimidine A and a WG formulation containing 750 g cyprodinil per kg. The observed and expected efficacies with different rates are given in Table V:

Table V

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine A	cyprodinil		
10	0	33	--
1	0	0	--
0	1	46	--
0	0.1	2	--
10	1	66	64
10	0.1	61	34
1	0.1	3	2

#### Example 6

**[0063]** Fungicidal efficacy of the mixture of Azolopyrimidine A + benomyl (3 day residual) against *Botrytis cinerea* on apple fruits

The tank mix was obtained from technical material of Azolopyrimidine A and a WP formulation containing 500 g benomyl per kg. The observed and expected efficacies with different rates are given in Table VI:

Table VI

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine A	benomyl		
10	0	25	--
1	0	0	--
0	10	13	--
0	1	0	--
10	10	87	35
10	1	38	25
1	10	35	13
1	1	15	0

#### Example 7

**[0064]** Fungicidal efficacy of the mixture of Azolopyrimidine A + vinclozolin (3 day residual) against *Botrytis cinerea* on apple fruits

The tank mix was obtained from technical material of Azolopyrimidine A and a WG formulation containing 500 g vinclozolin per kg. The observed and expected efficacies with different rates are given in Table VII:

Table VII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine A	Vinclozolin		
10	0	25	--
1	0	0	--
0	10	17	--
0	1	0	--
10	10	57	38
1	1	4	0

Example 8

[0065] Fungicidal efficacy of the mixture of Azolopyrimidine C + metconazole (1 day residual) against *Rhynchosporium secalis* on barley

The tank mix was obtained from technical materials of Azolopyrimidine C and metconazole. The observed and expected efficacies are given in Table VIII:

Table VIII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	metconazole		
100	0	15	--
0	100	87	--
100	100	100	89

Example 9

[0066] Fungicidal efficacy of the mixture of Azolopyrimidine C + metconazole (1 day residual) against *Septoria tritici* on wheat

The tank mix was obtained from a SC formulation containing 100 g Azolopyrimidine C per liter and an EC containing 100 g metconazole per liter. The observed and expected efficacies with different rates are given in Table IX:

Table IX

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	metconazole		
40	0	91	--
25	0	68	--
8	0	0	--
5	0	0	--
2	0	0	--
0	25	0	--
0	10	0	--
0	8	0	--
0	5	0	--
0	2	0	--
40	10	92	91
25	25	89	68
8	2	11	0
5	5	16	0
2	8	28	0

Example 10

[0067] Fungicidal efficacy of the mixture of Azolopyrimidine C + metconazole (1 day residual) against *Pyrenophora teres* on barley

The tank mix was obtained from a SC formulation containing 100 g Azolopyrimidine C per liter and an EC containing 100 g metconazole per liter. The observed and expected efficacies with different rates are given in Table X:

Table X

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	Metconazole		
125	0	0	--

Table X (continued)

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	Metconazole		
50	0	0	--
40	0	0	--
25	0	0	--
10	0	0	-
0	200	73	--
0	125	68	--
0	40	34	--
0	25	9	-
0	10	4	--
125	125	69	68
50	200	82	73
25	25	46	9
40	10	9	4
10	40	51	34

Example 11

**[0068]** Fungicidal efficacy of the mixture of Azolopyrimidine C + metconazole (1 day residual) against Puccinia recondita on wheat

The tank mix was obtained from from a SC formulation containing 100 g Azolopyrimidine C per liter and an EC containing 100 g metconazole per liter. The observed and expected efficacies with different rates are given in Table XI:

Table XI

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	metconazole		
200	0	35	--
125	0	20	--
40	0	10	--
25	0	5	--
10	0	3	--
8	0	1	--
2	0	2	--
0	125	97	--
0	50	72	--
0	40	31	--
0	25	14	--
0	10	8	--
0	8	0	--
0	2	0	--
200	50	86	82
125	125	99	98
40	10	25	17
25	25	22	18
10	40	70	33
8	2	1	1
2	8	8	2

Example 12

**[0069]** Fungicidal efficacy of the mixture of Azolopyrimidine C + kresoxim methyl (1 day curative) against Puccinia recondita on wheat

Plants sprayed twice, once with each compound. The tank mixes were obtained from a SC formulation containing 100 g Azolopyrimidine C per liter and a WG containing 500 g kresoxim methyl per kg. The observed and expected efficacies with different rates are given in Table XII:

Table XII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	kresoxim methyl		
400	0	99	--
200	0	97	--
100	0	79	--
50	0	66	--
25	0	25	--
0	400	5	--
0	200	1	--
0	100	0	--
0	50	1	--
0	25	0	--
400	400	99	99
200	200	94	97
100	100	86	79
50	50	84	66
25	25	29	25

Example 13

**[0070]** Fungicidal efficacy of the mixture of Azolopyrimidine C + carboxin (1 day residual) against Puccinia recondita on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and a WP formulation containing 750 g carboxin per kg. The observed and expected efficacies with different rates are given in Table XIII :

Table XIII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	carboxin		
4	0	100	--
1	0	71	--
0.25	0	41	--
0.06	0	8	--
0	4	4	--
0	1	0	--
0	0.25	0	--
0	0.06	0	--
4	4	100	100
1	1	89	71
0.25	0.25	66	49
0.06	0.06	59	8

Example 14

**[0071]** Fungicidal efficacy of the mixture of Azolopyrimidine C + fluazinam (1 day residual) against *Puccinia recondita* on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and a SC formulation containing 500 g fluazinam per liter. The observed and expected efficacies with different rates are given in Table XIV:

Table XIV

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	fluazinam		
4	0	100	--
1	0	71	--
0.06	0	8	--
0	4	17	--
0	1	4	--
0	0.06	0	--
4	4	100	100
1	1	92	72
0.06	0.06	24	8

Example 15

**[0072]** Fungicidal efficacy of the mixture of Azolopyrimidine C + quinoxifen (1 day residual) against *Puccinia recondita* on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and quinoxifen. The observed and expected efficacies with different rates are given in Table XV:

Table XV

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	quinoxifen		
4	0	100	--
1	0	71	--
0.25	0	49	--
0.06	0	8	--
0	4	0	--
0	1	0	--
0	0.25	0	--
0	0.06	0	--
4	4	100	100
1	1	95	71
0.25	0.25	54	49
0.06	0.06	23	8

Example 16

**[0073]** Fungicidal efficacy of the mixture of Azolopyrimidine C + quinoxifen (1 day residual) against *Blumeria graminis* on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and quinoxifen. The observed and expected efficacies with different rates are given in Table XVI:

Table XVI

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	quinoxifen		
4	0	96	--
1	0	42	--
0.25	0	19	--
0.06	0	0	--
0	4	99	--
0	1	73	--
0	0.25	18	--
0	0.06	8	--
4	4	100	100
1	1	87	85
0.25	0.25	53	33
0.06	0.06	24	8

Example 17

**[0074]** Fungicidal efficacy of the mixture of Azolopyrimidine C + metalaxyl (1 day residual) against *Blumeria graminis* on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and metalaxyl. The observed and expected efficacies with different rates are given in Table XVII:

Table XVII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	metalaxyl		
4	0	96	--
1	0	42	--
0.25	0	19	--
0.06	0	0	--
0	4	0	--
0	1	0	--
0	0.25	0	--
0	0.06	0	--
4	4	92	96
1	1	45	42
0.25	0.25	34	19
0.06	0.06	21	0

Example 18

**[0075]** Fungicidal efficacy of the mixture of Azolopyrimidine C + famoxadone (1 day residual) against *Blumeria graminis* on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and famoxadone. The observed and expected efficacies with different rates are given in Table XVIII:

Table XVIII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	Famoxadone		
4	0	96	--
1	0	42	--
0.25	0	19	--
0.06	0	0	--
0	4	0	--
0	1	0	--
0	0.25	0	--
0	0.06	0	--
4	4	96	96
1	1	53	42
0.25	0.25	34	19
0.06	0.06	9	0

Example 19

**[0076]** Fungicidal efficacy of the mixture of Azolopyrimidine C + famoxadone (1 day residual) against Puccinia recondita on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and famoxadone. The observed and expected efficacies with different rates are given in Table XIX:

Table XIX

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	famoxadone		
4	0	100	--
1	0	71	--
0.25	0	49	--
0.06	0	8	--
0	4	61	--
0	1	31	--
0	0.25	0	--
0	0.06	0	--
4	4	100	100
1	1	87	80
0.25	0.25	52	49
0.06	0.06	29	8

Example 20

**[0077]** Fungicidal efficacy of the mixture of Azolopyrimidine C + dodine (1 day residual) against Puccinia recondita on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and a WP containing 650 g dodine per kg. The observed and expected efficacies with different rates are given in Table XX:

Table XX

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	dodine		
0.06	0	8	--
0	0.06	0	--
0.06	0.06	28	8

Example 21

**[0078]** Fungicidal efficacy of the mixture of Azolopyrimidine C + copper oxychloride (1 day residual) against Puccinia recondita on wheat. The tank mix was obtained from technical material of Azolopyrimidine C and a WP containing 450 g copper oxychloride per kg. The observed and expected efficacies with different rates are given in Table XXI:

Table XXI

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	copper oxychloride		
0.06	0	8	--
0	0.06	0	--
0.06	0.06	18	8

Example 22

**[0079]** Fungicidal efficacy of the mixture of Azolopyrimidine C + sulfur (1 day residual) against Puccinia recondita on wheat

The tank mix was obtained from technical material of Azolopyrimidine C and sulfur. The observed and expected efficacies with different rates are given in Table XXII:

Table XXII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	sulfur		
1	0	71	--
0	1	0	--
1	1	86	71

Example 23

**[0080]** Fungicidal efficacy of the mixture of Azolopyrimidine C + triforine (1 day residual) against Erysiphe cichoracearum on cucumbers

The tank mix was obtained from a SC formulation containing 100 g of Azolopyrimidine C per liter and an DC formulation containing 190 g of triforine per liter. The observed and expected efficacies with different rates are given in Table XXIII:

Table XXIII

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	triforine		
4	0	7	--
1	0	0	--
0	16	15	--

Table XXIII (continued)

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	triforine		
0	4	0	--
4	16	47	34
1	4	12	0

**Example 24**

[0081] Fungicidal efficacy of the mixture of Azolopyrimidine C + cyprodinil (1 day residual) against *Erysiphe cichoracearum* on cucumbers. The tank mix was obtained from a SC formulation containing 100 g of Azolopyrimidine C per liter and a WG formulation containing 750 g of cyprodinil per kg. The observed and expected efficacies with different rates are given in Table XXIV:

Table XXIV

dose rate (ppm)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	cyprodinil		
4	0	7	--
1	0	0	--
0	16	29	--
0	4	0	--
4	16	41	34
1	4	10	0

**Example 25**

[0082] Fungicidal efficacy of the mixture of Azolopyrimidine C and different fungicides (1 day residual) against *Alternaria solani* on tomatoes. The tank mix was obtained from an SC formulation containing 100 g Azolopyrimidine A per liter and WP formulations of dithianon (750 g/kg), captan (500 g/kg), cyprodinil (750 g/kg), mancozeb (800 g/kg), or a SC formulation of chlorothalonil (500 g/l), or a FS formulation of fenpiclonil (400g/l), respectively. The observed and expected efficacies with different rates are given in Table XXV:

Table XXV

Azolopyrimidine C (g / ha)	Cereal Fungicide	rate (g / ha)	Observed Efficacy	Expected Efficacy
4	--	0	25	--
0	dithianon	16	50	--
0	captan	16	18	--
0	cyprodinil	16	13	--
0	mancozeb	16	27	--
0	chlorothalonil	16	13	--
0	fenpiclonil	16	76	--
4	dithianon	16	76	63
4	captan	16	60	38
4	cyprodinil	16	50	35
4	mancozeb	16	62	45
4	chlorothalonil	16	57	35
4	fenpiclonil	16	91	82

Example 26

**[0083]** Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C in admixture with Fenhexamid (2 days curative) against *Blumeria graminis* on barley.

The tank mixes were obtained from technical material of (S)-Azolopyrimidine C and Fenhexamid. The active ingredients, the observed and expected efficacies with different rates are given in Table XXVI:

Table XXVI

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	180	86	
	60	60	
	20	37	
	6.7	29	
	2.2	8	
	0.74	0	
Fenhexamid	180	39	
	60	7	
	20	1	
	6.7	0	
	2.2	0	
	0.74	0	
(S)-Azolopyrimidine C + Fenhexamid	180 + 180	95	91
	60 + 60	70	63
	20 + 20	42	38
	6.7 + 6.7	36	29
	2.2 + 2.2	18	8
	0.74 + 0.74	8	0

Example 27

**[0084]** Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C in admixture with Azoxystrobin or Trifloxystrobin (2 days curative) against *Blumeria graminis* on wheat.

The tank mixes were obtained from technical material of (S)-Azolopyrimidine C and Azoxystrobin or Trifloxystrobin. The active ingredients, the observed and expected efficacies with different rates are given in Table XXVII:

Table XXVII

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	50	81	
	25	61	
	12.5	40	
	6.3	10	
	3.1	0	
	1.6	0	
Azoxystrobin	50	61	
	25	48	
	12.5	28	
	6.3	21	
	3.1	2	
	1.6	0	
Trifloxystrobin	50	99	
	25	98	

Table XXVII (continued)

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
	12.5	89	
	6.3	78	
	3.1	55	
	1.6	34	
(S)-Azolopyrimidine C + Azoxystrobin	50 + 50	95	93
	25 + 25	79	80
	12.5 + 12.5	62	57
	6.3 + 6.3	30	29
	3.1 + 3.1	20	2
	1.6 + 1.6	14	0
(S)-Azolopyrimidine C + Trifloxystrobin	50 + 50	100	100
	25 + 25	100	99
	12.5 + 12.5	93	93
	6.3 + 6.3	75	80
	3.1 + 3.1	67	55
	1.6 + 1.6	45	34

Example 28

[0085] Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C in admixture with Azoxystrobin or Trifloxystrobin (2 days curative) against *Puccinia recondita* on wheat.

The tank mixes were obtained from technical material of (S)-Azolopyrimidine C and Azoxystrobin or Trifloxystrobin. The active ingredients, the observed and expected efficacies with different rates are given in Table XXVIII:

Table XXVIII

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	25	54	
	12.5	23	
	6.3	8	
	3.1	0	
	1.6	0	
Azoxystrobin	25	95	
	12.5	85	
	6.3	48	
	3.1	25	
	1.6	0	
Trifloxystrobin	25	0	
	12.5	0	
	6.3	0	
	3.1	0	
	1.6	0	
(S)-Azolopyrimidine C + Azoxystrobin	25 + 25	99	98
	12.5 + 12.5	87	88
	6.3 + 6.3	81	52
	3.1 + 3.1	45	25
	1.6 + 1.6	18	0
(S)-Azolopyrimidine C + Trifloxystrobin	25 + 25	53	54
	12.5 + 12.5	36	23

Table XXVIII (continued)

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
	6.3 + 6.3	15	8
	3.1 + 3.1	5	0
	1.6 + 1.6	0	0

Example 29

**[0086]** Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C in admixture with Azoxystrobin or Trifloxystrobin (2 days curative) against *Blumeria graminis* on barley.

The tank mixes were obtained from technical material of (S)-Azolopyrimidine C and Azoxystrobin or Trifloxystrobin. The active ingredients, the observed and expected efficacies with different rates are given in Table XXIX:

Table XXIX

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	50	73	
	25	54	
	12.5	31	
	6.3	15	
	3.1	1	
	1.6	0	
Azoxystrobin	50	87	
	25	73	
	12.5	49	
	6.3	21	
	3.1	10	
	1.6	0	
Trifloxystrobin	50	96	
	25	89	
	12.5	74	
	6.3	59	
	3.1	36	
	1.6	22	
(S)-Azolopyrimidine C + Azoxystrobin	50 + 50	98	96
	25 + 25	90	88
	12.5 + 12.5	75	65
	6.3 + 6.3	51	33
	3.1 + 3.1	18	11
	1.6 + 1.6	1	1
(S)-Azolopyrimidine C + Trifloxystrobin	50 + 50	100	99
	25 + 25	98	95
	12.5 + 12.5	87	82
	6.3 + 6.3	61	65
	3.1 + 3.1	46	37
	1.6 + 1.6	28	22

Example 30

**[0087]** Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C in admixture with Azoxystrobin or Trifloxystrobin (4 days residual) against *Blumeria graminis* on wheat.

The tank mixes were obtained from technical material of (S)-Azolopyrimidine C and Azoxystrobin or Trifloxystrobin.

The active ingredients, the observed and expected efficacies with different rates are given in Table XXX:

Table XXX

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	50	34	
	25	11	
	12.5	3	
	6.3	0	
	3.1	0	
Azoxystrobin	50	9	
	25	9	
	12.5	7	
	6.3	0	
	3.1	0	
Trifloxystrobin	50	14	
	25	0	
	12.5	0	
	6.3	0	
	3.1	0	
(S)-Azolopyrimidine C + Azoxystrobin	50 + 50	49	40
	25 + 25	25	19
	12.5 + 12.5	18	10
	6.3 + 6.3	1	0
	3.1 + 3.1	0	0
(S)-Azolopyrimidine C + Trifloxystrobin	50 + 50	51	43
	25 + 25	27	11
	12.5 + 12.5	29	3
	6.3 + 6.3	7	0
	3.1 + 3.1	9	0

#### Example 31

**[0088]** Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C in admixture with Azoxystrobin or Trifloxystrobin (4 days residual) against *Puccinia recondita* on wheat.

The tank mixes were obtained from technical material of (S)-Azolopyrimidine C and Azoxystrobin or Trifloxystrobin. The active ingredients, the observed and expected efficacies with different rates are given in Table XXXI:

Table XXXI

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	50	50	
	25	27	
	12.5	16	
	6.3	9	
	3.1	0	
Azoxystrobin	50	8	
	25	0	
	12.5	0	
	6.3	0	
	3.1	0	
Trifloxystrobin	50	0	

Table XXXI (continued)

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
	25	0	
	12.5	0	
	6.3	0	
	3.1	0	
(S)-Azolopyrimidine C + Azoxystrobin	50 + 50	63	54
	25 + 25	28	27
	12.5 + 12.5	21	16
	6.3 + 6.3	10	9
	3.1 + 3.1	6	0
(S)-Azolopyrimidine C + Trifloxystrobin	50 + 50	59	50
	25 + 25	35	27
	12.5 + 12.5	15	16
	6.3 + 6.3	10	9
	3.1 + 3.1	1	0

Example 32

[0089] Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C in admixture with Azoxystrobin (4 days residual) against *Blumeria graminis* on barley. The tank mixes were obtained from technical material of (S)-Azolopyrimidine C and Azoxystrobin. The active ingredients, the observed and expected efficacies with different rates are given in Table XXXII:

Table XXXII

Compound	dose rate (ppm)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	50	28	
	25	22	
	12.5	17	
	6.3	8	
	3.1	3	
	1.6	0	
Azoxystrobin	50	9	
	25	2	
	12.5	3	
	6.3	3	
	3.1	3	
	1.6	0	
(S)-Azolopyrimidine C + Azoxystrobin	50 + 50	39	34
	25 + 25	34	24
	12.5 + 12.5	27	19
	6.3 + 6.3	20	11
	3.1 + 3.1	20	6
	1.6 + 1.6	14	0

B Field TestsExample 33

[0090] Fungicidal efficacy of the mixture of Azolopyrimidine B + pyrimethanil in the field against *Botrytis cinerea* in vines

The tank mix was obtained from a SC formulation containing 100 g of Azolopyrimidine B per liter and a SC formulation containing 400 g of pyrimethanil per liter. The observed and expected efficacies are given in Table XXXIII:

Table XXXIII

dose rate g / ha		Observed Efficacy	Expected Efficacy
Azolopyrimidine B	pyrimethanil		
250	0	58	--
0	500	66	--
250	500	92	86

Example 34

**[0091]** Fungicidal efficacy of the mixture of Azolopyrimidine C + metconazole in the field against Septoria tritici on wheat

The tank mix was obtained from an EC formulation containing 150 g Azolopyrimidine C per liter and a SL formulation containing 60 g metconazole per liter. The observed and expected efficacies with different rates are given in Table XXXIVa (19 days after application) and Table XXXIVb (25 days after application):

Table XXXIVa

dose rate (g / ha)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	Metconazole		
25	0	48	--
0	15	9	--
0	30	36	--
0	45	24	--
25	15	73	53
25	30	74	67
25	45	76	60

Table XXXIVb

dose rate (g / ha)		Observed Efficacy	Expected Efficacy
Azolopyrimidine C	Metconazole		
50	0	61	--
75	0	13	--
0	15	33	--
0	60	48	--
50	15	82	74
75	60	66	55

Example 35

**[0092]** Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C + kresoxim methyl in the field against Septoria tritici on wheat

The tank mix was obtained from a SC formulation containing 100 g (S)-Azolopyrimidine C per liter and a WG formulation containing 500 g kresoxim methyl per kg. The observed and expected efficacies with different rates are given in Tables XXXVa (7 days after application), XXXVb (22 days after application), XXXVc (34 days after application), and XXXVd (41 days after application):

Table XXXVa

dose rate (g / ha)		Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	kresoxim methyl		
25	0	34	--
0	100	40	--
25	100	70	60

Table XXXVb

dose rate (g / ha)		Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	kresoxim methyl		
25	0	74	--
100	0	87	--
0	100	64	--
25	100	92	87
100	100	99	96

Table XXXVc

dose rate	(g / ha)	Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	kresoxim methyl		
50	0	53	--
100	0	70	--
0	50	44	--
0	100	59	--
50	100	88	83
100	50	84	83
100	100	92	88

Table XXXVd

dose rate (g / ha)		Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	kresoxim methyl		
75	0	92	--
0	100	92	--
75	100	100	98

**Example 36**

**[0093]** Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C + cyproconazole in the field against *Blumeria graminis* on wheat 17 days after application

The tank mix was obtained from a SC formulation containing 100 g (S)-Azolopyrimidine C per liter and an EC formulation containing 60 g cyproconazole per liter. The observed and expected efficacies with different rates are given in Table XXXVI:

Table XXXVI

dose rate (g / ha)		Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	cyproconazole		
25	0	63	--
50	0	78	--
75	0	74	--
0	15	86	--
0	30	82	--
25	15	96	95
25	30	98	93
50	30	100	96
75	30	98	95

Example 37

[0094] Fungicidal efficacy of the mixture of (S)-Azolopyrimidine C + azoxystrobin in the field against *Blumeria graminis* on wheat 17 days after application. The tank mix was obtained from a SC formulation containing 100 g (S)-Azolopyrimidine C per liter and a SC formulation containing 250 g azoxystrobin per kg. The observed and expected efficacies with different rates are given in Table XXXVII:

Table XXXVII

dose rate (g / ha)		Observed Efficacy	Expected Efficacy
(S)-Azolopyrimidine C	Azoxystrobin		
25	0	63	--
50	0	78	--
75	0	74	--
100	0	96	--
0	75	49	--
25	75	92	81
50	75	94	89
75	75	92	86
100	75	100	98

Example 38

[0095] Fungicidal efficacy of the mixture of Azolopyrimidine A and different cereal fungicides in the field against *Blumeria graminis* on wheat 15 days after application.

The tank mix was obtained from an SC formulation containing 100 g Azolopyrimidine A per liter and commercially available formulations of metconazole, epoxiconazole or kresoxim methyl, respectively. The observed and expected efficacies with different rates are given in Table XXXVIII:

Table XXXVIII

Azolopyrimidine A	Cereal Fungicide	rate (g / ha)	Observed Efficacy	Expected Efficacy
125	--	0	22	--
0	metconazole	45	54	--
0	epoxiconazole	63	40	--
0	kresoxim methyl	100	85	--
125	metconazole	45	79	64
125	epoxiconazole	63	74	53

Table XXXVIII (continued)

Azolopyrimidine A	Cereal Fungicide	rate (g / ha)	Observed Efficacy	Expected Efficacy
125	kresoxim methyl	100	92	88

**Example 39**

**[0096]** Fungicidal efficacy of the mixture of Azolopyrimidine A and different cereal fungicides in the field against *Septoria tritici* on wheat 15 days after application

The tank mix was obtained from an SC formulation containing 100 g Azolopyrimidine A per liter and commercially available formulations of metconazole, epoxiconazole or propiconazole, respectively. The observed and expected efficacies with different rates are given in Table XXXIX:

Table XXXIX

Azolopyrimidine A	Cereal Fungicide	rate (g / ha)	Observed Efficacy	Expected Efficacy
125	--	0	63	--
0	metconazole	45	77	--
0	epoxiconazole	63	93	--
0	propiconazole	63	72	--
125	metconazole	45	99	91
125	epoxiconazole	63	97	97
125	propiconazole	63	93	90

**Example 40**

**[0097]** Fungicidal efficacy of the mixture of Azolopyrimidine A and different cereal fungicides in the field against *Puccinia recondita* on wheat 50 days after application

The tank mix was obtained from an SC formulation containing 100 g Azolopyrimidine A per liter and commercially available formulations of metconazole, epoxiconazole, propiconazole or kresoxim methyl, respectively. The observed and expected efficacies with different rates are given in Table XXXX:

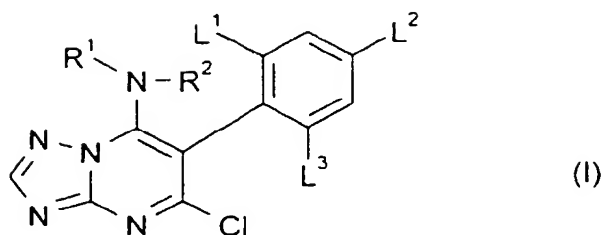
Table XXXX

Azolopyrimidine A	Cereal Fungicide	rate (g / ha)	Observed Efficacy	Expected Efficacy
125	--	0	0	--
0	metconazole	45	75	--
0	epoxiconazole	63	95	--
0	propiconazole	63	49	--
0	kresoxim methyl	100	0	--
125	metconazole	45	85	75
125	epoxiconazole	63	97	95
125	propiconazole	63	67	49
125	kresoxim methyl	100	64	0

**Claims**

1. A fungicidal composition comprising a fungicidally acceptable carrier and/or surface active agent and synergistically effective amounts of

(a) at least one azolopyrimidine of formula I



in which

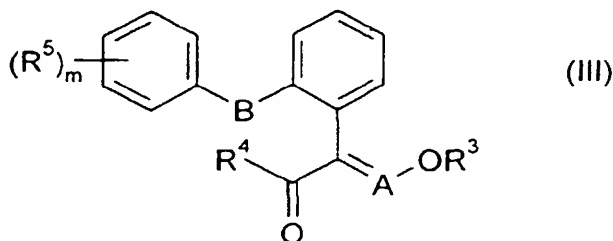
R<sup>1</sup> represents a C<sub>1-6</sub> alkyl, C<sub>3-6</sub> alkenyl or C<sub>1-6</sub> haloalkyl group, and  
 R<sup>2</sup> represents a hydrogen atom or a C<sub>1-6</sub> alkyl group, or  
 R<sup>1</sup> and R<sup>2</sup> taken together represent a C<sub>3-8</sub> alkylene group;  
 L<sup>1</sup> represents a halogen atom; and  
 L<sup>2</sup> and L<sup>3</sup> each independently represent a hydrogen or a halogen atom; and

(b) at least one fungicidal active ingredient selected from the following groups (A), (B) and (C):

(A) a compound selected from the group consisting of benomyl, carboxin, captan, chlorothalonil, copper oxychloride, cyprodinil, dimethomorph, dithianon, dodine, famoxadone, fenhexamid, fenpiclonil, fenpropimorph, fluazinam, mancozeb, metalaxyl, pyrimethanil, quinoxifen, sulfur, triforine and vinclozolin;  
 (B) a fungicidal triazole derivative; and  
 (C) a synthetic strobilurine derivative.

2. A composition as claimed in claim 1, wherein the triazole derivative (B) is selected from the group consisting of cyproconazole, epoxiconazole, metconazole, propiconazole and tebuconazole.

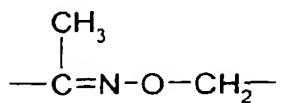
3. A composition as claimed in claim 1, wherein the synthetic strobilurine derivative is a compound of formula III,



wherein

A represents N or CH;

B represents a -O-, -OCH<sub>2</sub>-, a -CH<sub>2</sub>O-, a pyrimid-4,6-dioxydiyl group or a group of formula

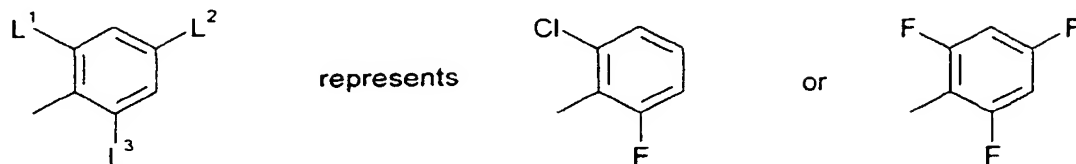


R<sup>3</sup> represents a C<sub>1-4</sub> alkyl group;

R<sup>4</sup> represents a C<sub>1-6</sub> alkoxy or a C<sub>1-6</sub> alkylamino group;

R<sup>5</sup> represents a hydrogen or halogen atom or a cyano, a C<sub>1-4</sub> alkyl or a C<sub>1-4</sub> haloalkyl group; and  
 m 0, 1 or 2.

4. A composition as claimed in claim 1 wherein in the compound of formula I



5. A composition as claimed in claim 4, wherein the azolopyrimidine is selected from the group consisting of:

15 5-chloro-6-(2-chloro-6-fluorophenyl)-7-(4-methylpiperid-1-yl)-[1,2,4]triazolo[1,5-a]pyrimidine,  
5-chloro-6-(2-chloro-6-fluorophenyl)-7-(2,2,2-trifluoroethylamino)-[1,2,4]triazolo[1,5-a]pyrimidine, and  
5-chloro-6-(2,4,6-trifluorophenyl)-7-(1,1,1-trifluoroprop-2-ylamino)-[1,2,4]triazolo[1,5-a]pyrimidine.

6. A composition as claimed in claim 3, wherein the strobilurine derivative is selected from azoxystrobin, trifloxystrobin and kresoxim methyl.

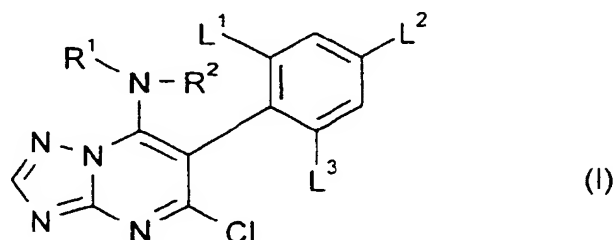
7. A composition as claimed in claim 1, wherein the ratio (by weight) of the fungicidal compound (b) to the azolopyrimidine of formula I (a) is approximately from 0.01 : 1 to 100 : 1.

8. A method of controlling the growth of phytopathogenic fungi at a locus which comprises applying synergistically effective amounts of (a) at least one azolopyrimidine of formula I as defined in claim 1 and (b) at least one at least one fungicidal active ingredient as defined in claim 1, to the locus.

9. A method of controlling wheat leaf rust, wheat Septoria leaf blotch and/or wheat powdery mildew which comprises applying synergistically effective amounts of at least one azolopyrimidine of formula I and at least one at least one fungicidal active ingredient selected from the groups (A), (B) and (C), as defined in claim 1 to the locus.

10. A fungicidal composition comprising a fungicidally acceptable carrier and/or surface active agent and synergistically effective amounts of

(c) at least one azolopyrimidine of formula I



in which

R<sup>1</sup> represents a C<sub>1-6</sub> alkyl, C<sub>3-6</sub> alkenyl or C<sub>1-6</sub> haloalkyl group, and

R<sup>2</sup> represents a hydrogen atom or a C<sub>1-6</sub> alkyl group, or

R<sup>1</sup> and R<sup>2</sup> taken together represent a C<sub>3-8</sub> alkylene group;

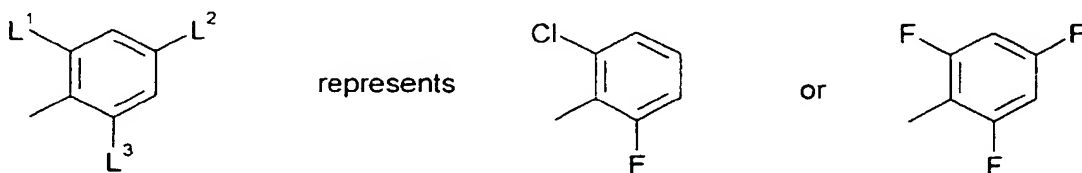
L<sup>1</sup> represents a halogen atom; and

L<sup>2</sup> and L<sup>3</sup> each independently represent a hydrogen or a halogen atom; and

(d) at least one fungicidal active ingredient selected from the following groups (A), (B) and (C):

- (A) a compound selected from the group consisting of benomyl, carboxin, captan, chlorothalonil, copper oxychloride, cyprodinil, dimethomorph, dithianon, dodine, famoxadone, fenpiclonil, fenpropimorph, fluazinam, mancozeb, metalaxyl, pyrimethanil, quinoxifen, sulfur, triforine and vinclozolin;  
 (B) a fungicidal triazole derivative; and  
 (C) a synthetic strobilurine derivative.

11. A composition as claimed in claim 10 wherein in the compound of formula I



12. A composition as claimed in claim 11, wherein the azolopyrimidine is selected from the group consisting of:

- 20
- 5-chloro-6-(2-chloro-6-fluorophenyl)-7-(4-methylpiperid-1-yl)-[1,2,4]triazolo[1,5-a]pyrimidine,  
 5-chloro-6-(2-chloro-6-fluorophenyl)-7-(2,2,2-trifluoroethylamino)-[1,2,4]triazolo[1,5-a]pyrimidine, and  
 5-chloro-6-(2,4,6-trifluorophenyl)-7-(1,1,1-trifluoroprop-2-ylamino)-[1,2,4]triazolo[1,5-a]pyrimidine.

13. A composition as claimed in claim 10, wherein the ratio (by weight) of the fungicidal compound (b) to the azolopyrimidine of formula I (a) is approximately from 0.01 : 1 to 100 : 1.

14. A method of controlling the growth of phytopathogenic fungi at a locus which comprises applying synergistically effective amounts of (a) at least one azolopyrimidine of formula I as defined in claim 10 and (b) at least one at least one fungicidal active ingredient as defined in claim 10, to the locus.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 99 30 7521

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,A	US 5 593 996 A (PEES KLAUS-JURGEN ET AL) 14 January 1997 (1997-01-14) * column 1, line 35 - line 65 * * column 4, line 3 - line 4 * * column 8, line 34 - line 36 * ---	1-14	A01N43/90 //(A01N43/90, 59:20,59:02, 47:44,47:38, 47:14,47:04, 43:84,43:76, 43:653,43:60, 43:54,43:42, 43:40,43:36, 43:32,37:50, 37:38,37:34, 37:22)
P,A	US 5 948 783 A (COTTER HENRY VAN TUYL ET AL) 7 September 1999 (1999-09-07) * column 2, line 39 - line 56 * * column 4, line 25 - line 26 * * column 9, line 54 - column 10, line 36 * * example 1 * ---	1-14	
P,A	WO 98 46607 A (AMERICAN CYANAMID CO) 22 October 1998 (1998-10-22) * page 3, line 5 - line 15 * * page 17, line 14 - page 18, line 19 * * page 21; example 28 * -----	1-14	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			A01N
Place of search		Date of completion of the search	Examiner
THE HAGUE		22 December 1999	Lamers, W
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 82 (pub.01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 7521

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-12-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5593996 A	14-01-1997	AT 159256 T	15-11-1997
		AU 667204 B	14-03-1996
		AU 3043592 A	01-07-1993
		BR 9205172 A	06-07-1993
		CA 2086404 A	01-07-1993
		CN 1075144 A, B	11-08-1993
		CN 1141119 A	29-01-1997
		DE 69222746 D	20-11-1997
		DE 69222746 T	12-02-1998
		DK 550113 T	09-02-1998
		EP 0550113 A	07-07-1993
		EP 0782997 A	09-07-1997
		ES 2108727 T	01-01-1998
		GR 3025920 T	30-04-1998
		IL 104244 A	13-07-1997
		JP 5271234 A	19-10-1993
		NZ 245581 A	26-07-1995
		PL 174047 B	30-06-1998
		PL 171579 B	30-05-1997
		RU 2089552 C	10-09-1997
		SG 47563 A	17-04-1998
		ZA 9210043 A	28-07-1993
US 5948783 A	07-09-1999	NONE	
WO 9846607 A	22-10-1998	AU 6576898 A	11-11-1998

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82